United States Patent [19]
St. Clair et al.

[11] **4,395,540**
[45] **Jul. 26, 1983**

[54] **THERMOSET-THERMOPLASTIC AROMATIC POLYAMIDE CONTAINING N-PROPARGYL GROUPS**

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[21] Appl. No.: **199,768**

[22] Filed: **Oct. 23, 1980**

[51] **Int. Cl.**[3] **C08G 69/26**

[52] **U.S. Cl.** **528/345;** 525/420; 528/183; 528/192; 528/220; 528/336

[58] **Field of Search** 528/345; 525/426

[56] **References Cited**

U.S. PATENT DOCUMENTS

4,097,456 6/1978 Barie 525/426

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[57] **ABSTRACT**

A novel composition and method for increasing the use temperature of polyamides based on the incorporation of a latent crosslinking agent into the polymer backbone, wherein high temperature performance is achieved without sacrificing solubility or processability.

7 Claims, No Drawings

THERMOSET-THERMOPLASTIC AROMATIC POLYAMIDE CONTAINING N-PROPARGYL GROUPS

ORIGIN OF THE INVENTION

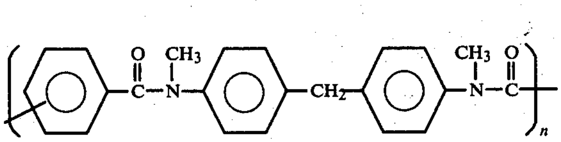
The invention described herein was made jointly by an employee of the U.S. Government and under a NASA contract and is subject to the provisions of Section 305 of the National Aeronautics and Space Act of 1958, Public Law 85-568 (72 Stat. 435; USC 2457).

BACKGROUND OF THE INVENTION

The use of thermoplastics such as polyamides as matrix resins for use in composite or laminate fabrication has one major drawback, they must be processed at and have a heat distortion temperature (HDT) of at least 50° C. above the temperature at which they are to be used so that their modulus or stiffness properties will be acceptable. This problem becomes compounded when an organic fiber is to be used as the reinforcing agent with such a polymer because the fiber also has a characteristic temperature at which it begins to irreversibly lose its stiffness properties. This is generally due to a relaxation phenomenon occurring in a highly oriented fiber.

The case in point is where the fiber to be utilized (of the aromatic polyamide class) in a structural composite application has a relaxation that occurs slightly below 300° C. In order to fabricate a structural laminate with this fiber reinforcement a temperature of 280° C. should not be exceeded in order to assure maximum fiber modulus. This thermal restriction must now in turn be imposed on the resin or polymer meaning it should be processable at a temperature lower than 280° C.

Attempts to develop a polymer which would be thermally and chemically compatible with the fiber led to the development of an aromatic secondary polyamide of the following recurring structure:



This polymer had the necessary property of a low HDT (154° C.), but the problem still existed of not being able to utilize the full thermal potential of the fiber (300° C.) because the polymer would soften at the lower temperature. The heating of this polymer to temperatures approaching the relaxation temperature of the fiber had no effect on the polymer's HDT.

There is thus a definite need in the art for an aromatic or aliphatic polyamide resin that can be cured in the region of 300° C. and have a HDT no more than 50°-70° C. below this temperature.

Accordingly, an object of the present invention is to develop a polyamide which can be processed at or below 300° C. due to a low HDT and then subsequently attain a higher HDT due to a chemical conversion which occurs during the thermal treatment.

Another object of the present invention is a novel polyamide which can be utilized for fabricating structural composites.

Another object of the present invention is a novel polyamide or series of polyamides which can be utilized as thermoset-thermoplastics due to a latent chemical conversion.

Another object of the present invention is a novel process of preparing a thermoset-thermoplastic molding material.

Another object of the present invention is a novel process for fabricating a structural composite which is solvent resistant.

Another object of the present invention is a novel process for fabricating structure composites.

Another object of the present invention is a novel polymer which is soluble before thermal processing, but solvent resistant after this processing.

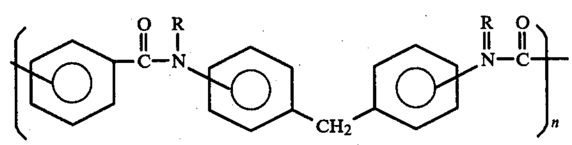
SUMMARY OF THE INVENTION

According to the present invention, the foregoing and other objects are attained by incorporating a latent crosslinking moiety at various levels along the backbone of an aromatic polyamide in order to produce a polymer of high molecular weight which will soften to allow processing at a relatively low temperature (154° C.) and subsequently "set-up" when treated at a higher temperature (280° C.). This type system may be referred to as a thermoplastic-thermoset resin since it initially behaves like a conventional thermoplastic and subsequently set-up through latent crosslinking sites.

These sites of latent crosslinking from the basis for the present invention. These sites were necessitated by processing restrictions not to enter into any chemical reactions during the fabrication of the thermoplastic component, and then, on heating to a more elevated temperature to form crosslinks which in turn results in a polymer system with an increased HDT and also increased resistance to solvents.

DETAILED DESCRIPTION OF THE INVENTION

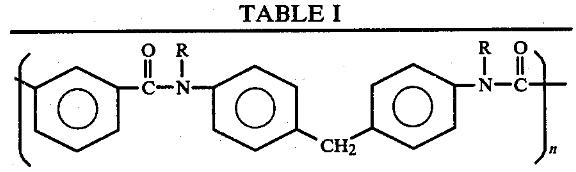
The structure of the novel system of the present invention is:



where R in a given unit is —CH_3 and —CH_2—C≡CH in varying ratios from where —CH_3 is 99% and —CH_2C≡CH is 1% to where —CH_3 is 0% and —CH_2C≡CH is 100%.

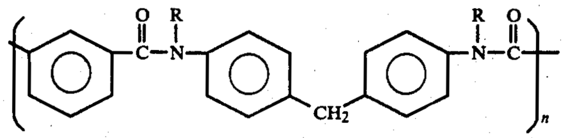
In the above structure it is the —CH_2C≡CH or propargyl group that is the latent crosslinking agent which increases the polymers HDT and solvent resistance. Table I illustrates the polymers HDT change as the progargyl group is increased for the following polymer

TABLE I



R	HDT, after treatment to 280° C. for 15 min., °C.
(1) 100% —CH_3, 0% —CH_2—C≡CH	(Control Composition) 165

TABLE I-continued



R	HDT, after treatment to 280° C. for 15 min., °C.
(2) 99% $—CH_3$, 1% $—CH_2—C≡CH$	171
(3) 95% $—CH_3$, 5% $—CH_2—C≡CH$	193
(4) 90% $—CH_3$, 10% $—CH_2—C≡CH$	200
(5) 67% $—CH_3$, 33% $—CH_2—C≡CH$	206

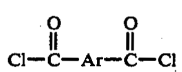
The improvement in solvent resistance was proven by immersing the polyamide (1) which contained no propargyl and (4) which contained 10% propargyl into various solvents after treating to 280° C. for 15 minutes. The results were as follows:

TABLE II

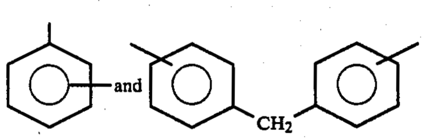
	Percent Propargyl in Polymer	
Solvent	0%	10%
Chloroform	Soluble	Swelling of polymer only
Cresol Mixture	Soluble	Swelling of polymer only

The reaction of the propargyl group was monitored by infrared spectroscopy by following the disappearance of the ≡C—H absorption at 3.1 microns (wavelength) or 3025 cm^{-1} (frequency). The exotherms for the reaction of the propargyl were also monitored by differential scanning calorimetry (DSC). The exotherm in the DSC spectrum for propargyl occurred between 200°-350° C. generally centered at approximately 300° C. (maximum rate of reaction).

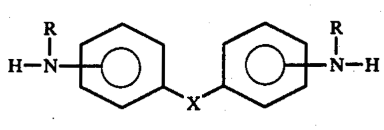
The polyamides were all prepared by a conventional method where an aromatic diacid chloride of the general formula



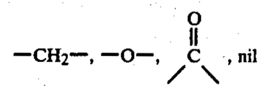
where Ar is selected from



is allowed to react with a bis-secondary aromatic diamine of the general formula



where X is selected from



and R is selected from $—CH_3$ and $—CH_2C≡CH$ in a solvent such as sym tetrachloroethane.

The propargyl containing aromatic diamines were prepared by the N,N'-dialkylation of primary aromatic diamines.

EXPERIMENTAL DETAILS

Preparation of p,p'-Bis(trifluoroacetamido)diphenylmethane

Trifluoroacetic anyhydride (105.0 g, 0.50 mol) was slowly added to 40.0 g (0.20 mol) of p,p'-diaminodiphenylmethane in 300 ml of tetrahydrofuran. The reaction mixture was refluxed 1.5 hours, then the solvent was stripped by rotary evaporation. The crude tan solid was recrystallized from chloroform/methanol to yield 77.32 g (99% yield) of the desired product, mp 229°-230° C.

Preparation of N,N'-Bispropargyl-p,p'-bis(trifluoroacetamido)diphenylmethane

To 3.7 g (0.154 mol) of sodium hydride in 20 ml of N,N'-dimethylformamide was added 20.0 g (0.0513 mol) of the trifluoroacetomide from the previous reaction. The resulting yellow dianion solution was filtered through a glass frit and 24.41 g (0.205 mol) of propargyl bromide was added. The reaction mixture was allowed to stir at room temperature for eight hours. The reaction mixture was poured into 1 N HCl and the resulting oil was extracted with ethyl acetate, dried with $MgSO_4$, and concentrated. Flash chromatography gave 20.08 g (84% yield) of the desired product mp 153°-155° C.

Preparation of N,N'-Bispropargyl-p,p'-diaminodiphenylmethane

Powdered potassium hydroxide (0.93 g, 0.0166 mol) was added to a slurry of 1.94 g (0.004 mol) of N,N'-bispropargyl-p,p'-bis(trifluoroacetamido)diphenylmethane in 100 ml of 95% ethanol. This solution was stirred at room temperature for one hour, then poured into cold water causing the crude product to precipitate. This material was recrystallized from 95% ethanol to give 1.05 g (92% yield) of the bispropargyl compound, mp 107°-108° C.

Typical Procedure for Polymerizing a Bisproparyldiamine with a Diacid Chloride

Appropriate molar portions (0.02 mol total) of diamines were weighed into a 50 ml resin kettle and dissolved in 20-25 ml of dry $CHCl_3$ (distilled from CaH_2 after initial washing with H_2O to remove $EtOH^3$ stabilizer). Dry, powdered Ca (0.08 mol) was then added, and the reaction mixture stirred to achieve a homogeneous slurry. To the vigorously stirred suspension was added dropwise a solution of 0.02 mol of isophthaloyl chloride (ICL) in 10 ml of $CHCl_3$. The reaction mixture was cooled with an ice bath to maintain the temperature at 25° C. When addition of the ICL was complete, the addition funnel was rinsed with 5 ml of $CHCl_3$, which was then added to the reaction flask. At this point the reaction mixture normally had appreciable viscosity,

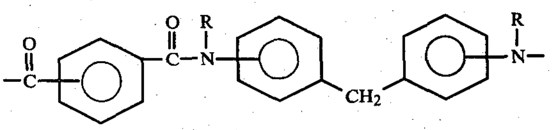
and was allowed to stir at room temperature for 0.5 hour, heating briefly at reflux (15 min.), and then either stirred overnight or worked up immediately if the solution was very viscous. In some instances the extended reaction period seemed to increase the viscosity of the solution.

The polymer was diluted to a volume of 125 ml with $CHCl_3$ and filtered through a coarse-fritted funnel to remove most of the CaO. The slightly cloudy filtrate was transferred to a separatory funnel and extracted with dilute HCl, washed with water, dried ($MgSO_4$) and concentrated to 100 ml. At this point the $CHCl_3$ solution was quite viscous and colorless. White, fibrous polymer was then obtained by precipitation when the solution was poured slowly into either petroleum ether or hexane in a blender. The polymer was filtered, washed with petroleum ether, air dried, and then dried in vacuo at 100° C. overnight.

The above specific examples are considered illustrative of the invention and there may be modifications and variations therein that will be apparent to those skilled in the art without departing from the spirit and scope of the invention as set forth herein.

What is claimed as new and desired to be secured by Letters Patent of the United States is:

1. A solvent stable thermosetting polyamide having improved heat distortion temperature characteristics and comprising repeating units of the formula:



wherein R represents a mixture of —CH_3 and —CH_2—C≡CH in varying percentages.

2. The polyamide of claim 1 wherein the percentage of —CH_3 ranges from zero to 99% and the percentage of —CH_2—C≡CH ranges from 1% to 100%.

3. The polyamide of claim 1 wherein the percentage of repeating units having R representing —CH_3 is 99% and the percentage of repeating units having R representing —CH_2—C≡CH is 1%.

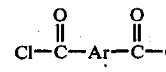
4. The polyamide of claim 1 wherein the percentage of repeating units having R representing —CH_3 is 95% and the percentage of repeating units having R representing —CH_2—C≡CH is 5%.

5. The polyamide of claim 1 wherein the percentage of repeating units having R representing —CH_3 is 90% and the percentage or repeating units having R representing —CH_2—C≡CH is 10%.

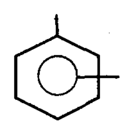
6. The polyamide of claim 1 wherein the percentage of repeating units having R representing —CH_3 is 67% and the percentage of repeating units having R representing —CH_2—C≡CH is 33%.

7. A process of preparing the polyamide of claim 1 comprising:

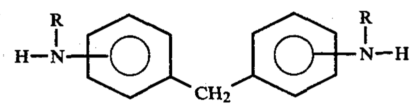
reacting (1) a diacid chloride of the formula:



wherein Ar is:



with (2) a bis-secondary diamine of the general formula:



wherein R represents a mixture of —CH_3 and —CH_2—C≡CH in varying percentages.

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